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(54) Title: BLOOMING TYPE, HARD SURFACE CLEANING AND/OR DISINFECTING COMPOSITIONS (57) Abstract Blooming type, hard surface cleaning concentrate compositions feature substantially reduced amounts of pine oil, or contain no pine oil. The cleaning concentrates exhibit a characteristic bloom when admixed to a larger volume of water, yet are substantially clear and shelf stable as concentrate compositions.		

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BLOOMING TYPE, HARD SURFACE CLEANING AND/OR DISINFECTING COMPOSITIONS

5 The present invention is directed to improved hard surface cleaning compositions and concentrates thereof, which feature blooming when the concentrate is added to a larger volume of water.

Cleaning compositions are commercially important products and enjoy a wide field of utility in assisting in the removal of dirt and grime from surfaces, especially those characterized as useful with
10 "hard surfaces". One particular category of cleaning compositions are those which are classed as pine oil type cleaning compositions which typically contain a significant amount, e.g, 5%wt. of naturally derived and/or synthetically produce pine oils. Such compositions generate a milky or cloudy appearance when diluted with water in dilutions useful for cleaning applications, and are generally provided as concentrated composition which is subsequently diluted with water by an end user/consumer
15 to form a cleaning composition therefrom. While such pine oil type cleaning compositions are commercially significant and in popular use, their use is not without attendant shortcomings. For example, high levels of pine oil in a cleaning composition are known to leave undesirable surface residues, particularly on hard surfaces. Also, such pine oils require the inclusion of surfactants which are useful in solubilizing and stabilizing the pine oil. Also, frequently the pine oil itself, are categorized
20 as undesired volatile organic compounds ("VOC"). However, the removal of the pine oil itself is not desired nor in most case feasible as its presence is associated with the formation of the blooming effect when the concentrate is added to a larger volume of water. This blooming effect (also sometimes referred to as "break" in the United Kingdom and in other countries) is an important indicia for consumer acceptance for certain products, those which traditionally use pine oil to providing the
25 blooming effect, as well as other products which do not contain pine oil but which nonetheless exhibit this very desirable blooming behavior when added to a larger volume of water to form a cleaning and/or disinfecting composition therefrom.

Therefore, there exist a need in the art for the production of blooming type hard surface cleaning compositions, including pine oil type cleaners, which exhibit the desirable blooming characteristics
30 expected by the consumer, but in which little or no pine oil need be present. Such compositions would contain no pine oil, or would contain significantly reduced amounts of pine oil as compared to known art compositions. There is also a need in the art for blooming type hard surface cleaning compositions which provide a cleaning, as well as germicidal effect to a treated surface.

In accordance with a first aspect of the present invention, there has been made the surprising
35 discovery that successful blooming type hard surface cleaners may be produced which do not include pine oil, but which nonetheless exhibits the much desired blooming behaviour which is associated with

pine oil cleaners. This surprising discovery now permits for the production of concentrate compositions which are transparent or relatively clear in appearance, but which when added to a greater volume of water such as to form a cleaning and/or disinfecting composition therefrom, exhibits a blooming behaviour. This discovery permits for the production of cleaning and/or disinfecting compositions and concentrates thereof which contain no pine oil, yet which exhibit this important identifying characteristics of pine oil type cleaning compositions. This discovery also permits for the production of aqueous cleaning and/or disinfecting compositions which exhibit blooming when added to a larger volume of water, but which may be selectively imparted with any of a number of different appearances and fragrances which is possible by the judicious selection of any of a number of dyes, fragrances, other colorants which may be added to the concentrate compositions to provide a desired color and a desired scent. Such compositions are commercially acceptable, shelf stable concentrated cleaning and/or disinfecting compositions which exhibit blooming when diluted in water. According to this first aspect of the invention, the blooming behaviour is provided although the concentrate compositions contain no pine oil or pine oil fraction (such as a terpineol fraction) in any significant amount, other than minor amounts such as might be used in a fragrance constituent, as the compositions do not rely upon pine oil or pine oil fractions to provide their blooming characteristic when diluted with water. Accordingly there are provided aqueous blooming type, hard surface cleaning and/or disinfecting concentrate compositions which comprise the following essential constituents which provide a "blooming system" which is incorporated in these compositions:

- a cationic quaternary ammonium surfactant;
- an anionic carboxylated alcohol alkoxylate surfactant;
- a surfactant compatibilizing agent; and,
- water.

According to this first inventive aspect, the concentrate compositions may include further optional constituents which do not undesirably reduce or which diminish the operation of the blooming system described herein especially one or more further surfactants including anionic, cationic, nonionic, zwitterionic and/or amphoteric as well as mixtures thereof, one or more organic solvents such as lower alkyl alcohols, lower alkyl diols and glycol ethers, as well as one or more fragrances, coloring agents, chelating agents, germicidal compositions including those based on phenolic compounds, as well as other conventional additives.

Such compositions according to the first aspect of the invention exhibit the desired "blooming" characteristic of pine oil type cleaners, but do not require the presence of pine oil to provide the blooming effect. Rather, selected known art dyes or other coloring agents, in conjunction with minor amounts of one or more fragrance materials especially those which provide a pine type scent may be

included to the blooming system, as well as further optional surfactants and or organic solvents which are included to provide a deterative property to the compositions. In this way, a cleaning composition which has the physical appearance and blooming characteristic of a conventional pine oil type cleaning composition may be provided without the presence of pine oil. Similarly, other blooming type cleaning and/or disinfecting compositions may be produced such as by including different fragrances, i.e., those characteristic of lemon, various flora, in conjunction with a desired coloring additives, i.e., green, yellow, amber, red, etc. may be added as desired. In each case, a blooming type cleaning and/or disinfecting compositions may produced. "Blooming" may be described as the change of the water's appearance from essentially colorless and transparent to that of a milky white or milky yellowish white, cloudy appearance. Also, in the concentrate compositions according to any aspect of the invention, the lack of the overall amounts of pine oil typically found in prior art pine oil type cleaning concentrates, as well as the necessary compatibilizing agents required to solubilize the pine oil in such prior art cleaning concentrate provides the benefits of reduced volatile organic content of a concentrate or cleaning composition, as well as reduces the propensity of such compositions to form undesirable residues, especially pine oil residues upon cleaned surfaces.

In a second aspect of the invention, there is provided a blooming, pine oil type hard surface cleaning composition which has reduced amounts of pine oil as compared to known art pine oil containing compositions which include the following essential constituents:
The compositions according to this second aspect of the invention comprises the following constituents on a percentage weight basis based on a 100%wt. concentrate composition:

pine oil in an amount of from 0.01 - 3%wt., preferably 0.01 - 2.5% by weight, but most preferably 0.75-1.5%wt.l;

at least one pine oil solubilizing agent in an amount of to 15% and less by weight, preferably 0.01-10% by weight, and most preferably in an amount of 0.1-5% by weight

and the blooming system as described with respect to the first aspect of the invention which blooming system includes:

a cationic quaternary ammonium surfactant;

an anionic carboxylated alcohol alkoxylate surfactant;

a surfactant compatibilizing agent; and,

water.

The compositions according to this second aspect of the invention the concentrate compositions may include further optional constituents which do not undesirably reduce or which diminish the operation of the blooming system described herein especially one or more further surfactants including anionic, cationic, nonionic, zwitterionic and/or amphoteric as well as mixtures thereof, one or more

organic solvents such as lower alkyl alcohols, lower alkyl diols and glycol ethers, as well as one or more fragrances, coloring agents, chelating agents, germicidal compositions including those based on phenolic compounds, as well as other conventional additives. The concentrate compositions according to the second aspect of the invention exhibit the desired "blooming" characteristic of pine oil type cleaners, although do not require the presence of pine oil to provide the blooming effect which is primarily provided by the blooming system previously described. These concentrate compositions are pine oil type cleaning compositions which include reduced amounts of pine oil as compared to known art compositions, and in preferred embodiments also provide a germicidal effect in both concentrate composition, and in cleaning composition dilutions.

In according to a third aspect of the invention, there is also provided a blooming, pine oil type hard surface cleaning composition with reduced amounts of pine oil. The compositions according to this second aspect of the invention comprises the following constituents on a percentage weight basis based on a 100%wt. concentrate composition:

pine oil, in amount of 0.1-5% by weight, preferably in amounts of 0.1 - 4% by weight, but most preferably in amount of between 2 - 4% by weight;

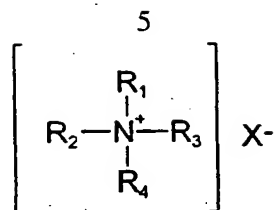
at least one pine oil solubilizing agent effective in enhancing the miscibility of the pine oil constituent in water which may be present in any effective amount found but desirably is present in amounts of up to about 15% by weight, preferably in amounts of 0.1 - 15% by weight, but most preferably from 5 - 15% by weight

a nonionic surfactant with a cloud point of 20°C or less; and, water.

The concentrate compositions according to the third aspect of the invention may include the same further optional constituents described in conjunction with the second aspect of the invention noted above. Similarly, the concentrate compositions in the third aspect of the invention provide pine oil type cleaning compositions with reduced amounts of pine oil as noted above, and in preferred embodiments also provide a germicidal effect.

In a still further aspect of the invention there are provided processes for cleaning and/or disinfecting hard surfaces by applying effective amounts of a cleaning composition as taught in this specification to a hard surface in need of cleaning and/or disinfection.

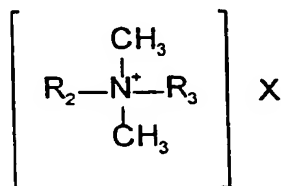
The at least one cationic quaternary ammonium surfactant useful in forming the blooming system according to the first and second aspects of the invention, and which may be used as an optional germicidal constituent in the second aspect of the invention may be any of those which are known to the art, but preferably are quaternary ammonium compounds and salts thereof. These include quaternary ammonium germicides which may be characterized by the general structural formula:



where at least one of R_1 , R_2 , R_3 and R_4 is a hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular weight of at least 165. The hydrophobic radicals may be long-chain alkyl, long-chain alkoxy aryl, long-chain alkyl aryl, halogen-substituted long-chain alkyl aryl, long-chain alkyl phenoxy alkyl, aryl alkyl, etc. The remaining radicals on the nitrogen atoms other than the hydrophobic radicals are substituents of a hydrocarbon structure usually containing a total of no more than 12 carbon atoms. The radicals R_1 , R_2 , R_3 and R_4 may be straight chained or may be branched, but are preferably straight chained, and may include one or more amide or ether linkages. The radical X may be any salt-forming anionic radical.

Exemplary quarternary ammonium salts within the above description include the alkyl ammonium halides such as cetyl trimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyl dimethyl benzyl ammonium bromide, N-alkyl pyridinium halides such as N-cetyl pyridinium bromide, and the like. Other suitable types of quarternary ammonium salts include those in which the molecule contains either amide or ether linkages such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, N-(laurylcocoaminoformylmethyl)-pyridinium chloride, and the like. Other very effective types of quarternary ammonium compounds which are useful as germicides include those in which the hydrophobic radical is characterized by a substituted aromatic nucleus as in the case of lauryloxyphenyltrimethyl ammonium chloride, cetylaminophenyltrimethyl ammonium methosulfate, dodecylphenyltrimethyl ammonium methosulfate, dodecylbenzyltrimethyl ammonium chloride, chlorinated dodecylbenzyltrimethyl ammonium chloride, and the like.

Preferred quarternary ammonium compounds which act as germicides and which are found useful in the practice of the present invention include those which have the structural formula:



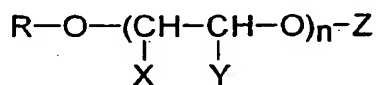
wherein R_2 and R_3 are the same or different C_8 - C_{12} alkyl, or R_2 is C_{12-16} alkyl, C_{8-18} alkylethoxy, C_{8-18} alkylphenoethoxy and R_3 is benzyl, and X is a halide, for example chloride, bromide or iodide, or methosulfate. The alkyl groups recited in R_2 and R_3 may be straight chained or branched, but are preferably substantially linear.

Such quaternary germicides are usually sold as mixtures of two or more different quaternaries, such as BARDAC® 205M, (presently commercially available from Lonza, Inc., Fairlawn, NJ) which is believed to be a 50% aqueous solution containing 20% by weight of an alkyl dimethyl benzylammonium chloride (50% C14, 40% C16 alkyl); 15% by weight of an octyl decyl dimethylammonium chloride; 7.5% by weight of dioctyl dimethylammonium chloride; and 7.5% by weight of didecyl dimethylammonium chloride. A further useful quaternary germicide is CYNICAL® 80% (presently commercially available from Hilton Davis Chemical Co., Cincinnati, OH) which is believed to comprise 80% by weight of an alkyl dimethyl benzylammonium chloride (50% C14, 40% C12 and 10% C16 alkyl), 10% water and 10% ethanol. Further useful quaternary germicidal agents include BTC-8358®, an alkyl benzyl dimethyl ammonium chloride (80% active), BTC-835® an alkyl benzyl dimethyl ammonium chloride (53% active), and BTC-818®, a dialkyl dimethyl ammonium chloride (commercially available from the Stepan Chemical Co., Chicago, IL). Additional suitable commercially available quaternary ammonium germicides of the alkyl dimethyl benzylammonium chloride type containing the same alkyl dimethyl benzylammonium chloride mixture as that of CYNICAL® and which are generally referred to as quaternium salts include BARQUAT® MB-80, (presently commercially available from Lonza, Inc., Fairlawn, NJ) which is believed to be an 80% by weight solution (20% ethanol) of the quaternary, HYAMINE® 1622 believed to be an aqueous solution of benzethonium chloride, and HYAMINE® 3500, which is believed to be a 50% aqueous solution of the quaternary (both presently commercially available from Lonza Inc., Fairlawn, NJ).

The cationic quaternary ammonium surfactant may be present in any amount which are found to exhibit the desirable characteristics according to a respective aspect of the invention; in the first or second aspect the surfactant forms part of the blooming system, and should be present in amounts wherein the concentrate compositions are relatively clear appearance in concentrated solution, but which exhibit blooming when diluted with further water to form a cleaning composition. In accordance with the third aspect of the invention, the addition of the preferred cationic quaternary ammonium surfactants which exhibits germicidal activity are included in preferred embodiments where a germicidal effect is intended to be provided by the compositions. The amounts in a respective composition are noted above, and it is to be noted that the preferred amounts are in part dictated by toxicological considerations as an excess of the cationic component may pose an increasing risk of irritation to the eyes, skin and mucocous tissues of a consumer. The preferred amounts are also in part dictated by economic considerations as an excess of the cationic component above these amounts generally requires a corresponding increase in the amount of the anionic component used in a blooming system as noted above.

In accordance with the first and second inventive aspects described above, there is also included at least one anionic carboxylated alcohol alkoxylate surfactant. This anionic surfactant which has been found to be effective in forming a water insoluble or poorly miscible complex when mixed with the quaternary ammonium compound described above, which due to said insolubility or poor miscibility of the formed complex, renders an aqueous mixture containing the anionic carboxylated alcohol alkoxylate surfactant and the quaternary ammonium compound such an aqueous mixture turgid, milky or cloudy.

Particularly useful carboxylated alcohol alkoxylate compounds which are advantageously incorporated into the compositions of the invention include carboxylated alcohol alkoxylate surfactants according to the following general formula:



wherein R is a hydrophobic group, more preferably a C₆-C₁₈ alkyl group, n is a number in the range of 1 to 24, X and Y are independently selected from the group consisting of hydrogen, succinic acid radical, hydroxysuccinic acid radical, citric acid radical, and mixtures thereof, wherein at least one of X or Y is a succinic acid radical, hydroxysuccinic acid radical, or citric acid radical, and Z is H or -CH₂COOH. Certain anionic surfactants according to the immediately preceding general formula are presently commercially available as the PolyTergent® C series of anionic surfactants from the Olin Chem. Co., (Stamford, CT). Particularly preferred amongst these are the PolyTergent™ CS-1 compounds which is believed to be in accordance with the formula above wherein R is a C₆-C₁₈ alkyl group, X and Y are independently H, CH₃ or the succinic acid radical with at least one succinic acid radical being present, and where Z is H. Also useful is PolyTergent™ C9-62P a further carboxylated alcohol alkoxylate surfactant also available from the Olin Chemical Co.

Other known anionic surfactants, while not particularly enumerated here may also find use in the present inventive compositions, as well as mixtures of one or more anionic surfactants.

According to the first and second aspects of the invention, the carboxylated alcohol alkoxylate is present in any amount which is found to exhibit the desirable characteristics of the invention, that of a relatively clear appearance in an aqueous solution when in the presence of an effective amount of the quaternary ammonium compound described above and further with an effective amount of the surfactant compatibilizing agent described below, but that of blooming when diluted with further water to form a cleaning composition. This anionic surfactant compound is included in the amounts noted above.

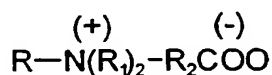
In the blooming system according to the first and second aspect of the invention described previously, particular attention is to be paid to the relative proportions of the cationic surfactant to the anionic surfactant. It is a feature of the invention that both the cationic quaternary ammonium surfactant and the anionic carboxylated alcohol alkoxylate surfactant, and surfactant compatibilizing agent be

present in such amounts such that the concentrate composition be relatively clear when present in the concentrate composition. Such a concentrate composition is relatively clear and is preferably transparent. However, upon the addition of the said concentrate composition to a further amount of water, the solubility of these cationic surfactants and the anionic surfactants in the new larger volume of water is sufficiently reduced or disrupted which causes the newly formed composition to become turgid, or cloudy and thus imitate the "blooming" behaviour of prior art pine oil cleaner type compositions. While not wishing to be bound by any theory, it is hypothesized that in the absence of a sufficient amount of the surfactant compatibilizing agent, the pendant carboxylic acid or carboxylic acid moieties of the preferred species of anionic surfactants effectively complex with the quarternary ammonium in the quarternary ammonium compound and become insoluble or immiscible in an aqueous mixture, which then become visible due to the presence of the sufficiently long alkyl chain moieties which also constitute part of the preferred anionic surfactants. This effect may however be reversed by the addition of an additional, sufficient amount of the surfactant compatibilizing agent to such a mixture, which addition solubilizes at least the anionic surfactant and/or the complexed cationic and anionic surfactants. Such solubilization effectively restores the clear appearance of the aqueous mixture containing the cationic and anionic surfactants. It is contemplated that other anionic surface active agents having a first functional portion or group effective in forming a complex with the quarternary ammonium compound in water, and which has a second functional portion or group which is hydrophobic in nature and which is insoluble or poorly miscible in water when such a complex is formed and in the absence of any further compatibilizing agent(s) become visible to the eye, may also be used.

In accordance with the first and second aspect of the invention, the blooming system includes a surfactant compatibilizing agent which solubilizes the at least one cationic quarternary ammonium surfactant and the at least one anionic carboxylated alcohol alkoxylate surfactant may be any known art material which exhibits the properties described above. A variety of surfactant compatibilizing agents are believed to be determinable by routine experimental techniques, such as by providing a volume of water having mixed therein amounts of the cationic quarternary ammonium surfactant compound and the anionic carboxylated alcohol alkoxylate surfactant compound which renders the volume of water to be non-transparent, especially turgid or milky in appearance, and adding thereto an amount of a compound or composition which may be used to compatibilize the anionic and cationic surfactant compounds. Afterwards, an aliquot of this mixture may then be added to a larger volume of water, such as a mixture:water dilution ratio of 1:64 at room temperature (approx. 20°C) to determine if such mixture evidences a blooming effect.

One class of such useful surfactant compatibilizing agents are water soluble salts including, but not limited to monovalent alkali and/or polyvalent alkaline earth metal salts and ammonium salts. Non-limiting examples of such useful salts include: NaCl, MgCl₂, NaHCO₃, Na₂CO₃, NH₄Cl.

A further class of useful surfactant compatibilizing agents include certain amphoteric surfactants. Useful amphoteric surfactants include betaine compounds which exhibit the following general formula:



wherein R is a hydrophobic group selected from the group selected from alkyl groups containing from about 10 to about 22 carbon atoms, preferably from about 12 to about 18 carbon atoms, alkylaryl and arylalkyl groups containing a similar number of carbon atoms with a benzene ring being treated as equivalent to about 2 carbon atoms, and similar structures interrupted by amido or ether linkages; each R₁ is an alkyl group containing from 1 to about 3 carbon atoms; and R₂ is an alkylene group containing from 1 to about 6 carbon atoms.

Examples of preferred betaines include lauramidopropyl betaine, a commercial preparation of which is available under the tradename Mirataine® BB (from Rhône-Poulenc, Cherry Hill, NJ), and cocamidopropyl betaine available under the trade name Mackam™ DZ (from McIntyre Group Ltd., University Park, IL).

As noted previously, effective amounts of the surfactant compatibilizing agent may be any amount which, when included in the blooming systems in the first and second aspects of the invention compatibilize in the concentrate composition dilution the least one cationic quaternary ammonium surfactant and the at least one anionic carboxylated alcohol alkoxylate surfactant, but do not diminish the blooming characteristic of the concentrate composition when it is added to water. The surfactant compatibilizing agent may be present in any effective amount, and good compatibilizing behaviour has been observed with amounts of 10% by weight and less, with preferred amounts being 0.01 - 6% by weight of the compatibilizing agent. While amount less than 6% are to be preferred from an economic standpoint, it is to be understood that other amounts, including those greater than 6% by weight may be necessitated due to the selected cationic surfactant, and anionic surfactant, their relative amounts used, and their miscibility in water.

In accordance with the third aspect of the invention, in the place of the blooming system according to the first and second aspects of the invention there is included one or more nonionic surfactants which are characterized in exhibiting a cloud point of 20°C or less. Suitable nonionic surface active agents include condensation products of one or more alkylene oxide groups with an organic hydrophobic compound, such as an aliphatic or alkyl aromatic compound. Suitable nonionic surface

active agents include surfactant compositions based upon polyethoxylated, polypropoxylated, or polyglycerolated alcohols or alkylphenols or fatty acids. It is contemplated that one or more nonionic surfactants which are characterized in exhibiting a cloud point of 20°C or less may also be used as the sole blooming agent in an aqueous hard surface cleaning and/or disinfecting composition, i.e., absent the pine oil discussed herein.

One exemplary class of nonionic surfactants which finds use are alkoxyated alcohols especially alkoxyated fatty alcohols. These include ethoxylated and propoxylated fatty alcohols, as well as ethoxylated and propoxylated alkyl phenols, having both with alkyl chains of about 7-16, more preferably about 8-13 carbon chains in length.

Exemplary alkoxyated alcohols include certain ethoxylated alcohol compositions presently commercially available from the Shell Chemical Company, (Houston, TX) under the general trade name Neodol®, which are described to be linear alcohol ethoxylates. Of these, those exhibiting a cloud point of 20°C or less may be used. Specific compositions include: Neodol® 91-2.5 which is described as an ethoxylated alcohol having an average molar ratio of 2.7:1 ethoxy groups/alcohol groups per molecule; a molecular weight of 281, and a cloud point in water of 20°C and less; Neodol® 23-3 which is described as an ethoxylated alcohol having an average molar ratio of 2.9:1 ethoxy groups/alcohol groups per molecule; a molecular weight of 322, and a cloud point in water of 20°C and less.

Exemplary alkoxyated alcohols further include certain compositions presently commercially available from the Union Carbide Co., (Danbury, CT) under the general trade name Tergitol®, which are described to be secondary alcohol ethoxylates. Again, those exhibiting a cloud point of 20°C and less may be used. Specific compositions include: Tergitol® 15-S-3 which is described as an ethoxylated secondary alcohol having an average molar ratio of 3.2:1 ethoxy groups/alcohol groups per molecule, and a cloud point in water of less than 20°C; Tergitol® 15-S-5 which is described to be an ethoxylated secondary alcohol having an average molar ratio of 5:1 ethoxy groups/alcohol groups per molecule, and a cloud point in water of less than 20°C.

Exemplary alkoxyated alkyl phenols include certain compositions presently commercially available from the Rhône-Poulenc Co., (Cranbury, NJ) under the general trade name Igepal®, which are described to be octyl and nonyl phenols. Again, those exhibiting a cloud point of 20°C or less may be used. Specific compositions include: Igepal® CA-210 which is described as an ethoxylated octyl phenol having an average of 1.5 ethoxy groups groups per molecule and a cloud point in water of less than 20°C and, Igepal® CA-420 which is described as an ethoxylated octyl phenol having an average of 3 ethoxy groups groups per molecule and a cloud point in water of less than 20°C.

Of course, a mixture of two or more nonionic surfactant compounds having a cloud point of 20°C or less may be incorporated into the inventive compositions. Other known nonionic surfactants not particularly enumerated here may also be used.

5 The cloud point of the nonionic surfactant may be determined by known methods. For example, ASTM D2024 (reapproved 1986) for "Standard Test method for Cloud Point of Nonionic Surfactants". According to this test method which is particularly useful for nonionic surfactants of a detergent systems which are characterized of less soluble in water at higher temperatures than at lower temperatures wherein the cloud point occurs within water at a temperature range of between 30-95°C. According the test protocol, a one percent test solution is prepared by weighing one gram of the surfactant into a 150
10 ml. beaker to which 100 mls. of distilled demineralized water at a temperature of less than 30°C is added. The sample is agitated until solution is reached, after which a 50 ml. aliquot of the solution is placed into a test tube. While agitating the sample solutions slowly with the thermometer, the test tube is heated with a bunsen burner until the sample solution becomes definitely cloudy, at which point it is removed from the heat. While stirring with the thermometer continues, the test tube and its sample
15 solution are allowed to cool slowly until the sample solution clarifies at which point the temperature is noted. Such a test method provides a simple, yet reliable, means for determining the cloud point of a surfactant in water.

An even simpler test method for effectively determining which nonionic surfactants may be used in the compositions of the invention is as follows: to a clean beaker or other glass vessel is added
20 99 parts by weight of deionized water at 20°C ±0.5°C, and 1 part by weight (by weight of the actives) of a surfactant composition to be tested. This test sample is stirred and the temperature permitted to drop to 20°C; if this test sample is observed to be murky or cloudy in appearance as the test sample's temperature achieves 20°C and drops below 20°C, it is considered to have a suitable cloud point of 20°C and less and may be used in the concentrate compositions according to this aspect of the invention.

25 In accordance with the third inventive aspect, such a nonionic surfactant may be present in any effective amount, but desirably is present in the concentrate compositions in amounts of up to about 10% by weight, preferably in amounts of 0.1 and 6% by weight, but most preferably in amount of between 4 and 6% by weight.

30 Water is included in the concentrate compositions and in order to provide 100% by weight of the concentrate composition. The water may be tap water, but is preferably distilled and/or deionized water. If the water is tap water, it is preferably appropriately filtered in order to remove any undesirable impurities such as organics or inorganics, especially minerals salts which are present in hard water which may thus interfere with the operation of one or more constituents of the blooming system, as well as any other optional components of the liquid concentrates according to the invention. Generally, water

is present in the concentrate compositions in amounts in excess of about 50% by weight, preferably in amounts of in excess of 70% by weight, but most preferably in amounts in excess of 80% by weight of the concentrate compositions according to the invention.

In accordance with the second and third aspects of the invention described above, there is also included as an essential constituent an amount of a pine oil constituent., while in the first aspect of the invention such a pine oil constituent is to be understood as an optional constituent.

Pine oil is a complex blend of oils, alcohols, acids, esters, aldehydes and other organic compounds, and is sometimes used as a solvent for certain types of stains. An important constituent of pine oil are terpene alcohols, especially alpha-terpineol. When included, the pine oil generally comprises at least about 60% terpene alcohols, especially alpha-terpineol. Particularly effective presently commercially available pine oils Glidco® Pine Oil™ 60 (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 60% terpene alcohols), Glidco® Pine Oil 60 (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 60% terpene alcohols); Glidco® Pine Oil 140 (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 70% terpene alcohols); Glidco® Pine Oil 80 (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 80% terpene alcohols) Glidco® Pine Oil 150 (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 85% terpene alcohols); Glidco® Terpene SW (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 75% terpene alcohols); as well as Glidco® Terpineol 350 (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 100% terpene alcohols). Other products which can contain up to 100% pure alpha-terpineol, may also be used in the present invention.

When included, the pine oil constituent need be present in only minor amounts as they are not required to produce the blooming characteristics of the inventive compositions. Generally, they are present in reduced amounts in any of the concentrate compositions, i.e., in amounts of up to about 3% by weight, and if present are preferably included in amounts of from 0.01 - 2.5% by weight, but most preferably in amount of between 0.75-1.5% pine oil by weight. As with all of the weight percentages of the constituents described, the weight percentages are indicative of the weight percentages of the actives in a constituent containing preparation.

Further in accordance with the second and third aspects of the invention, in addition to the pine oil constituent there is also included an effective amount of at least one pine oil solubilizing agent.

Exemplary pine oil solubilizing agents include certain nonionic alkoxyated linear alcohol surfactants which aid in the dissolution of the pine oil in the water of the concentrate composition. Such useful nonionic alkoxyated linear alcohol nonionic surfactants are known, and may be commercially obtained from the Olin Chemical Co., (Stamford, CT) under the product line name of "PolyTergent®".

Particular members of this product line which have been found useful include; PolyTergent® SL-42 and PolyTergent® SL-62. Further useful nonionic surfactants include alkoxylated linear secondary alcohols, as well as alkoxylated alkylphenolic nonionic surfactants. Such nonionic surfactants also provide a deterative effect to the compositions.

5 Further exemplary pine oil solubilizing agents include C₁-C₈ alcohols, especially C₁-C₃ alcohols, of which isopropanol is preferred.

The pine oil solubilizing agents are included in effective, often minor amounts, with specific preferred weight proportions having been described previously.

10 The compositions according to the first, second or third aspects of the invention in many cases which comprise any of a number of further optional constituents which do not undesirably reduce or which diminish the operation of the blooming system described herein especially one or more further surfactants including anionic, cationic, nonionic, zwitterionic and/or amphoteric as well as mixtures thereof, one or more organic solvents such as lower alkyl alcohols, lower alkyl diols and glycol ethers, as well as one or more fragrances, coloring agents, chelating agents, antioxidants, germicidal
15 compositions including those based on phenolic compounds, as well as other conventional additives. Such further optional constituents may be included in amounts found not to substantially interfere or detract from the blooming characteristics provided by the invention. Such materials are known to the art, and are described in *McCutcheon's Emulsifiers and Detergents (Vol. 1)*, *McCutcheon's Functional Materials (Vol. 2)*, North American Edition, 1991; *Kirk-Othmer, Encyclopedia of Chemical Technology*,
20 3rd Ed., Vol. 22, the contents of which are herein incorporated by reference.

Known surfactants which provide a further deterative effect to the concentrate compositions and especially to the cleaning compositions formed therefrom may be where such do not substantially interfere or detract from the blooming characteristics provided by the invention, and further desirably do diminish the germicidal nature of the preferred cationic quaternary ammonium compounds which are
25 included in the blooming system being taught herein. Such include anionic, cationic, nonionic, zwitterionic and/or amphoteric as well as mixtures thereof.

Useful anionic surfactants include the water-soluble salts, particularly the alkali metal, ammonium and alkylammonium (e.g., monoethanolammonium or triethanolammonium) salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from
30 about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of aryl groups.) Examples of this group of synthetic surfactants are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain.

Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 14.

Other anionic surfactants herein are the water soluble salts of: paraffin sulfonates containing from about 8 to about 24 (preferably about 12 to 18) carbon atoms; alkyl glyceryl ether sulfonates, especially those ethers of C₈₋₁₈ alcohols (e.g., those derived from tallow and coconut oil); alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 4 units of ethylene oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group; and alkyl ethylene oxide ether sulfates containing about 1 to about 4 units of ethylene oxide per molecule and from about 10 to about 20 carbon atoms in the alkyl group.

Other useful anionic surfactants herein include the water soluble salts of esters of α -sulfonated fatty acids containing from about 0 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and β -alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Care should be exercised however in the selection of the anionic surfactants as it is known to the art that many anionic form insoluble complexes with cationic quaternary ammonium surfactants, and their use in most cases is to be limited to minor amounts or wholly avoided.

Useful nonionic surfactants which may be included in the concentrate compositions include known art nonionic surfactant compounds. Such nonionic surfactant compounds provide a further deterative effect to the concentrate compositions and cleaning compositions formed therefrom. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a water soluble nonionic surfactant compound. Further, the length of the polyethenoxy hydrophobic and hydrophilic elements may various. Exemplary nonionic compounds include the polyoxyethylene ethers of alkyl aromatic hydroxy compounds, e.g., alkylated polyoxyethylene phenols, polyoxyethylene ethers of long chain aliphatic alcohols, the polyoxyethylene ethers of hydrophobic propylene oxide polymers, and the higher alkyl amine oxides.

To be mentioned as particularly useful nonionic surfactants are alkoxylated linear primary and secondary alcohols such as those commercially available under the tradenames PolyTergent® SL series (Olin Chemical Co., Stamford CT), Neodol® series (Shell Chemical Co., Houston TX); as alkoxylated alkyl phenols including those commercially available under the tradename Triton® X series (Union Carbide Chem. Co., Danbury CT). Also to be noted as useful are the nonionic surfactants discussed

above with regard to the third aspect of the invention, namely the essential nonionic surfactant constituent.

Known organic solvents which may be useful in providing a further cleaning benefit, especially in the loosening of stains may be added to the concentrate compositions of the invention. Such should be selected and be present in amounts which do not substantially interfere or detract from the blooming characteristics provided by the invention. Exemplary organic solvents include lower alkyl alcohols, lower alkyl diols and glycol ethers.

Lower alkyl alcohols which may be included are generally the water soluble C_1 - C_8 alcohols as well as the water miscible C_1 - C_8 diols examples of which include methanol, ethanol, propanol, isopropanol, butanol including t-butanol.

Exemplary glycol ethers water miscible glycol ethers including those having the general structure R_a -O- R_b -OH, wherein R_a is an alkoxy of 1 to 20 carbon atoms, or aryloxy of at least 6 carbon atoms, and R_b is an ether condensate of propylene glycol and/or ethylene glycol having from one to ten glycol monomer units. Preferred are glycol ethers having one to five glycol monomer units. These are C_3 - C_{20} glycol ethers. Examples of more preferred solvents include propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol isobutyl ether, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol butyl ether, diethylene glycol phenyl ether, propylene glycol phenol ether, and mixtures thereof. Further useful as the organic solvent are water-miscible ethers such as diethylene glycol diethylether, diethylene glycol dimethylether, propylene glycol dimethylether, as well as lower esters of monoalkylethers of ethyleneglycol or propylene glycol such as propylene glycol monomethyl ether acetate. Such are commercially available from Union Carbide, Dow Chemicals or Hoescht. Mixtures of organic solvents can also be used.

A further optional, but in some cases advantageous organic solvent which may be included are one or more terpene solvents, especially monocyclic monoterpene and bicyclic terpenes which include terpinene, terpinolene, limonene, pinene and mixtures thereof. Some may be found in fractions of pine oils noted above, but preferred are those which may be obtained from the essence of citrus fruits of various types including from oranges, lemons and grapefruit. These are generally mixtures which include one or more of the following: d-limonene, dipentene, alpha-pentene, beta-pinene of which d-limonene is most preferred and may for example be obtained by distilling orange rind oil. Such a material is readily commercially available, has a very pleasant citrus fragrance, is known to have favorable cleaning properties and is derived from a naturally occurring material. If present such materials, especially materials which comprise 90%wt. and greater of d-limonene, need be present in only minor amounts, i.e., about 7%wt. and less, preferably about 5%wt. and less, and preferably about 3%wt. and less of the concentrate composition.

Certain of the optional constituents, such as the derivatives of citrus fruit may be provided with, or benefit from the addition of minor amounts of a stabilizer such as an antioxidant material, such as butylated hydroxytoluene.

Further optional, but desirable constituent include fragrances, natural or synthetically produced
5 containing synthetic fragrance compositions, especially those which are intended to mimic the scent of one or more resins or oils derived from coniferous species of trees, viz., a scent characteristic of pine oil type cleaning concentrates as well as scents characteristic of other forms of flora, such as flowers. Other desired fragrance materials may also be included in the compositions, and such are generally included in minor amounts, i.e., less than about 5%wt. of a concentrate compositions and care should be exercised so
10 as not to undesirably inhibit the operation of the blooming system according to the invention and as described above. Many organic materials which providing a fragrancng effect may be used and these include those described at columns 9 - 11 of US Patent 5,336,445 the contents of which are herein incorporated by reference. Particularly with regard to non-pine oil containing concentrate compositions, such fragrances may be added in any conventional manner, admixing to a concentrate composition or
15 blending with other constituents used to form a concentrate composition, in amounts which are found to be useful to enhance or impart the desired scent characteristic to the concentrate composition, and/or to cleaning compositions formed therefrom. However, they should not be included in excessive amounts.

Further optional, but advantageously included constituents are one or more coloring agents which find use in modifying the appearance of the concentrate compositions and enhance their
20 appearance from the perspective of a consumer or other end user. Known coloring agents, may be incorporated in the compositions in effective amount to improve or impart to concentrate compositions an appearance characteristic of a pine oil type concentrate composition, such as a color ranging from colorless to a deep amber, deep amber yellow or deep amber reddish color. Other coloring agents, such as those which may impart a yellow color, such as may be associated with a lemon colored cleaning
25 composition, or other colors may also be included. Such a coloring agent or coloring agents may be added in any useful amount in a conventional fashion, i.e., admixing to a concentrate composition or blending with other constituents used to form a concentrate composition.

Still further conventional additives which may be included are one or more hydrotopes such as sodium toluene sulfonate and sodium cumene sulfonate; one or more antibacterial agents such as
30 orthobenzyl-para-chlorophenol although in preferred embodiments wherein the cationic quaternary ammonium compound has germicidal activity a further antibacterial agent is not normally required, detergent builder compositions, chelating agent especially useful as hard water ion sequestrants, as well as others. Each of such materials is generally only included in very minor amounts, i.e., each generally not exceeding 0.15%wt of the concentrate composition, but desirably even less.

Generally the total weight of such further conventional additives may comprise up to 30% by weight of a concentrated composition formulation, but preferably comprise not in excess of 15%wt., and are typically significantly less.

5 What is to be understood by the term "concentrate" and "concentrate composition" in this specification and claims is the pre-consumer dilution and composition of the cleaning composition which is the essentially the form of the product prepared for sale to the consumer or other end user. Such a consumer or other end user would then normally be expected to dilute the same with water to form a cleaning composition. It is to be understood however that nothing in this invention would bar its use as cleaning composition without any further dilution and it may be used in the concentrations in
10 which it was prepared for sale. Similarly, what is to be understood by the term "cleaning compositions" are the water diluted compositions which are expected to be prepared by the consumer or other end user by mixing a measured amount of the "concentrate" with water in order to form an appropriately diluted cleaning composition which is suitable for use in cleaning applications, especially in the cleaning of hard surfaces.

15 As generally denoted above, the formulations according to any of the aspects of the invention described above include both cleaning compositions and concentrates as outlined above which differ only in the relative proportion of water to that of the other constituents forming such formulations. While the concentrated form of the cleaning compositions find use in their original form, they are more frequently used in the formation of a cleaning composition therefrom. Such may be easily prepared by
20 diluting measured amounts of the concentrate compositions in water by the consumer or other end user in certain weight ratios of concentrate:water, and optionally, agitating the same to ensure even distribution of the concentrate in the water. As noted, the concentrate may be used without dilution, i.e., in concentrate:water concentrations of 1:0, to extremely dilute dilutions such as 1:10,000. Desirably, the concentrate is diluted in the range of 1:0.1 - 1:1000, preferably in the range of 1:1 - 1:500 but most
25 preferably in the range of 1:10 - 1:100. The actual dilution selected is in part determinable by the degree and amount of dirt and grime to be removed from a surface(s), the amount of mechanical force imparted to remove the same, as well as the observed efficacy of a particular dilution. Generally better results and faster removal is to be expected at lower relative dilutions of the concentrate in water.

Examples:

30 Evaluation of Cloud Points of non-ionic surfactant compositions:

An evaluation of the cloud point for Neodol® 91-2.5, a nonionic surfactant composition based on linear alcohol ethoxylates was evaluated according to the following protocol. To a clean glass beaker was added 99 parts by weight of deionized water at 20°C ±0.5°C, to which was subsequently added 1 part by weight (by weight of the actives) of a Neodol® 91-2.5 composition. This test sample was

stirred and the sample was immediately observed to be murky or cloudy in appearance. The sample was allowed to drop to 20°C and it was observed to remain in its cloudy form. The surfactant composition was considered to be useful as as the nonionic surfactant in the concentrate compositions according to the third aspect of the invention.

5 In a similar manner, the cloud point of Neodol® 23-6.5, a nonionic surfactant composition based on linear alcohol ethoxylates was evaluated. To a clean glass beaker was added 99 parts by weight of deionized water at 20°C ±0.5°C, to which was subsequently added 1 part by weight (by weight of the actives) of the Neodol® 23-6.5 composition. The test sample was stirred and the sample was observed to be clear and transparent in appearance. The sample was allowed to drop to 20°C and no change in its appearance was noted. The surfactant composition was considered not to be useful as as the nonionic surfactant in the third aspect of the invention.

Preparation of Example Formulations:

15 Exemplary concentrate composition formulations according to the first aspect of the invention were prepared in accordance with the following general procedure.

20 Into a suitably sized vessel, the following constituents were added in the sequence: water, cationic and anionic surfactant compositions of the blooming system, the surfactant compatibilizing agent, and then any remaining constituents. All of the constituents were supplied at room temperature, and mixing of the constituents was achieved by the use of a magnetic stirrer. These constituents were used "as is" as supplied from their respective supplier. Mixing, which generally lasted from 1 minute to 5 minutes, was maintained until the formulation attained uniform color and uniform clarity. The example formulations were readily pourable, and retained well mixed characteristics indicative of stability.

The exact compositions of the example formulations according to the first aspect of the invention are listed on Table 1A, below.

TABLE 1A: EXAMPLE FORMULATIONS			
	Example Formulation: (in % weight)		
Constituent:	Ex.1A	Ex.2A	Ex.3A
PolyTergent® CS-1	3.0	6.0	--
PolyTergent® C9-62P	--	--	4.0
BTC-8358	3.0	--	--
BTC-818	--	6.0	4.2
sodium chloride	2.0	--	--
Mackam® DZ	--	5.6	11.4
PolyTergent® SL-42	--	1.25	--
deionized water	to 100	to 100	to 100

PolyTergent® CS-1 is a polycarboxylated alcohol alkoxylate (50% active) available from Olin Chemical Corp.
 PolyTergent® C9-62P is a polycarboxylated alcohol alkoxylate (50% active) available from Olin Chemical Corp.
 BTC-835 is an alkyl benzyl dimethyl ammonium chloride (53% active) available from Stepan Chemical Co.
 BTC-818 is a dialkyl dimethyl ammonium chloride (50% active) available from Stepan Chemical Co.
 Mackam® DZ is cocoamidopropyl betaine (30% active) available from McIntyre Group Ltd.
 Poly-Tergent® SL-42 is a nonionic alcohol alkoxylate available from Olin Chemical Corp.

Exemplary concentrate composition formulations according to the second aspect of the invention were prepared in accordance with the general procedure outlined above, and are illustrated on Table 1B following.

TABLE 1B: EXAMPLE FORMULATIONS

TABLE 1B: EXAMPLE FORMULATIONS									
Constituent:	Example Formulation: (in % weight)								
	Ex.1B	Ex.2B	Ex.3B	Ex.4B	Ex.5B	Ex.6B	Ex.7B	Ex.8B	Ex.9B
Pine Oil 60	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	3.0
PolyTergent® SL-62	2.6	2.0	2.1	---	4.0	1.6	1.6	---	6.43
isopropyl alcohol	---	---	---	15	---	---	---	---	---
BTC 8358	1.5	1.5	1.5	1.5	1.9	2.5	1.2	1.5	1.5
BTC 818	0.6	0.6	0.6	0.6	---	---	0.6	0.6	0.6
PolyTergent® CS-1	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
sodium chloride	1.7	---	---	---	1.2	---	---	---	---
magnesium chloride hexahydrate	---	0.8	---	---	---	---	---	---	---
sodium bicarbonate	---	---	2.7	---	---	---	---	---	---
Mackam® DZ	---	---	---	5.3	---	4.8	5.3	7.9	5.3
deionized water	89.6	91.1	89.1	73.6	88.9	87.1	87.3	86.0	80.2

Pine Oil 60 is pine oil preparation available from the Glidden Co.

Pine Oil 60 is pine oil preparation available from the Glidden Co, comprising approx. 60% weight terpene alcohol(s).

PolyTergent® CS-1 is a polycarboxylated alcohol alkoxylate (50% active) available from Olin Chemical Corp.

BTC 8358 is an alkyl benzyl dimethyl ammonium chloride (80% active) available from Stepan Chemical Co.

BTC 818 is a dialkyl dimethyl ammonium chloride (50% active) available from Stepan Chemical Co.

Mackram® DZ is cocoamidopropyl betaine (30% active) available from McIntyre Group Ltd.

PolyTergent® SL-62 is a nonionic alcohol alkoxylate available from Olin Chemical Corp.

Comparative formulations according to the prior art and example formulations according to the third aspect of the invention were prepared in accordance with the following general procedure.

Into a suitably sized vessel, the following constituents were added in the sequence: water, pine oil, nonionic surfactants, other surfactants, pine oil solubilizing agent, and if present BTC-8358®, a quarternary ammonium compound preparation. All of the constituents were supplied at room temperature (approximately 20°C), mixing of the constituents was achieved by the use of a magnetic stirrer. Stirring, which generally lasted from approximately 2 minutes to approximately 5 minutes continued and was maintained while the particular formulation attained uniform color and uniform clarity or translucency. Each of the formulations exhibited the following physical characteristics: transparent appearance, light to medium yellowish amber color, and an appreciable pine oil odor. The exemplary compositions were readily pourable, and retained well mixed characteristics, demonstrating excellent shelf stability.

The exact compositions of the example formulations are listed on Table 1C, below wherein the values indicated for each of the formulations are indicative of weight percents of the respective constituent in the formulation.

TABLE 1C: FORMULATIONS					
	Comp.1	Comp.2	Ex.1C	Ex.2C	Ex.3C
<u>Constituent:</u>					
Pine Oil 60	8	4	4	4	4.1
Neodol 91-2.5	--	--	4	4.1	4.1
Neodol 23-6.5	4	4	4	9.0	6.3
BTC-8358	1.87	1.87	1.87	--	--
Mackam™ DZ	--	--	--	--	5.2
isopropanol (100%)	23.8	6.8	9.6	15.0	15.0
deionized water	62.32	83.32	76.52	62.32	83.32

Pine Oil 60 is a pine oil preparation available from the Glidco Organics Corp., Jacksonville, FL

BTC-8358 is an alkyl benzyl dimethyl ammonium chloride (80% active) available from Stepan Chemical Co.

Neodol® 91-2.5 is a nonionic surfactant composition based on linear alcohol ethoxylates featuring a cloud point < 20°C available from Shell Chemical Co., Houston TX.

Neodol® 23-6.5 is nonionic surfactant composition based on linear alcohol ethoxylates featuring a cloud point > 20°C available from Shell Chemical Co., Houston TX.

Mackam™ DZ is a surfactant composition containing cocoamidopropyl betaine

With reference to Table 1C, formulations designated as "Comp.1" and "Comp.2" are indicative of illustrative formulations which did not comprise the nonionic surfactant having a cloud point less than 20°C, while the formulations designated as "Ex.1C", "Ex.2C" and "Ex.3C" are formulations demonstrating the blooming feature according to the present invention, and considered with in the

present inventive scope. Each of these formulations appeared to be translucent and varying little in color.

The determination of the the amount of a solubilizing agent, isopropyl alcohol, required in order to clarify the formulations of Table 1C provides a useful indication of the amount of required organic solvents/compatabilizers which are required in typical concentrate formulations. The weight percent of isopropyl alcohol (100%) which was added to each of the formulations is also indicated on Table 1C.

A further formulation according to the third aspect of the invention was produced in which no pine oil was present, but in which the sole blooming agent was the nonionic surfactant having a cloud point less than 20°C, and is illustrated on Table 1D following:

TABLE 1D: FORMULATION	
<u>Constituent:</u>	<u>weight percent</u>
Neodol® 91-2.5	5.66
Neodol® 91-8	5.66
Dowanol® PM	5.66
deionized water	83.02

Neodol® 91-2.5 is a nonionic surfactant composition based on linear alcohol ethoxylates featuring a cloud point < 20°C available from Shell Chemical Co., Houston TX.

Neodol® 91-8 is a nonionic surfactant composition based on linear alcohol ethoxylates available from Shell Chemical Co., Houston TX.

Dowanol® PM is a propylene glycol methyl ether available from Dow Chemical Co., Midland, Michigan.

Although the formulation on Table 1D did not include any pine oil, significant blooming was observed when diluted into a greater volume of water at room temperature at a ratio of formulation:water of 1:64. No pine oil was present in the composition.

Evaluation of Example Formulations:

Each of the example formulations was used to prepare an aqueous diluted form therefrom at a concentration and dilution typical of conventionally used cleaning and/or disinfecting compositions useful in commercial/residential locations. These aqueous dilutions were simply prepared by pouring one part by weight of each example formulation of Table 1 into 63 parts by weight of tap water (1:64 by weight dilution) at 20°C and in some instances at 40°C.

In each case, the addition of an example formulation to the water was accompanied by a change in the appearance of the water from transparent to a translucent cloudy, whitish appearance.

These aqueous dilutions were prepared to evaluate the degree of light transmittance, a measure of the opacity as well as of the blooming of each of the aqueous dilutions. Certain of these aqueous dilutions were also evaluated to determine the antimicrobial efficacy of the aqueous dilution. The results

of the light transmittance evaluation was determined as a percentage of light transmitted through a sample of a particular aqueous dilution wherein the transmission of a like sample of water is assigned a percentage of 100%. Testing was performed by mixing a 5g aliquot of a particular example formulation with 315 g of tap water (with approx. 100 ppm hardness), after which the sample was mixed for 60 seconds and a transmittance reading at 620 nm wavelength was taken using a Brinkman model PC801 dipping probe colorimeter, which was set at 620 nm to determine the light transmission of each of the samples. Samples of each formulation at 20°C and in some cases, at 40°C were evaluated, as well as the reference (pure tap water) sample used to calibrate the colorimeter to the reference 100% light transmission sample outlined above. The resulting determined values, reported in Tables 2A, 2B and 2C (corresponding to the formulations on Tables 1A, 1B and 1C respectively) below provide an empirical evaluation, reported in percent transmittance ("%") of the degree of transparency of a diluted example formulation wherein 0% indicates complete opacity and 100% the transparency of a water sample as noted above. Accordingly, those results indicative of lower transmittance values identify samples exhibiting desirable turgid or cloudy appearances indicative of desirable blooming effects.

TABLE 2A: TEST RESULTS OF TABLE 1A FORMULATIONS	
	Blooming
Dilution of Example Formulation:	transmission at 20°C
Ex.1A	9.2 %
Ex.2A	9.7 %
Ex.3A	19.7 %

TABLE 2B: TEST RESULTS OF TABLE 1B FORMULATIONS		
	Blooming	
Dilution of Example Formulation:	transmission at 20°C	transmission at 40°C
Ex.1B	13.0 %	10.4 %
Ex.2B	10.0 %	8.2 %
Ex.3B	11.1 %	8.7 %
Ex.4B	15.8 %	13.1 %
Ex.5B	53.7 %	8.6 %
Ex.6B	15.4 %	7.8 %
Ex.7B	71.8 %	14.8 %
Ex.8B	35.6 %	100.2 %
Ex.9B	17.2 %	22.9 %

TABLE 2C: TEST RESULTS - LIGHT TRANSMITTANCE					
Formulation:	Comp.1	Comp.2	Ex.1C	Ex. 2C	Ex. 3C
<u>Light Transmittance:</u>					
%T at 20°C	60.5	99.4	35.5	21.9	26.8
%T at 40°C	34.2	97.2	37.1	28.1	37.9

As may be seen from the above, the formulations according to the invention provided excellent blooming characteristics, although containing little or no pine oil in their formulations. In certain formulations, the absence of pine oil, or its presence in reduced amounts also required a substantial reduction in pine oil solubilizing agents as compared to prior art pine oil cleaning compositions; many such agents are considered undesired VOC's and their use is desirably limited.

As can be seen from the results reported above, the exemplary formulations featured good blooming behaviour as cleaning composition, but were substantially clear in the form of concentrate compositions.

The antimicrobial efficacy of certain of prepared formulations were also evaluated against two representative bacterial species, *Salmonella choleraesuis* and *Staphylococcus aureus*. As is known in the art, each of these bacterial species is commonly found and is desirably removed or destroyed during a cleaning procedure of such environments.

Antimicrobial efficacy of the prepared formulations according to examples were evaluated generally in accordance with the standardized AOAC Use-Dilution test method based on AOAC Official Methods of Analysis Procedures 955.14 "Testing disinfectants against *Salmonella Choleraesuis*," and Procedure 955.15 "Testing disinfectants against *Staphylococcus Aureus*" (15th Edition, 1990, pages 135-137, Use Dilution Methods). The results reported on Table 3 indicate the proportion of the number of sample test tubes within which the organism remained alive after 10 minutes of exposure at 20°C over the total number of test tube samples used in testing the exemplary formulations of Table 1B for their germicidal activity.

TABLE 3		
Dilution of Example Formulation:	<u>Antimicrobial Efficacy</u>	
	<i>Staphylococcus aureus</i>	<i>Salmonella choleraesuis</i>
Ex.5B	1/60	1/60
Ex.6B	1/60	1/60
Ex.7B	0/30	0/30

As can be seen from the results reported above, the exemplary formulations featured good blooming behaviour and the tested formulations also showed good efficacy as germicidal agents.

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Generally it is expected that formulations which contain effective amounts of the quaternary ammonium cationic surfactant described above especially with respect to the first and second aspects of the invention and/or which include a germicidal active agent such as the phenolic compositions described above are useful in providing germicidal active compositions within the scope of the present inventive teaching.

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Claims:

1. An aqueous blooming type, hard surface cleaning composition concentrate comprises a blooming sytem which is selected from:

a blooming system which comprises an effective amount of each of a cationic quaternary ammonium surfactant; an anionic carboxylated alcohol alkoxylate surfactant; a surfactant compatibilizing agent; and, water,

or,

a blooming system comprising one or more nonionic surfactants which are characterized in exhibiting a cloud point of 20°C or less in water.

2. The composition according to claim 1 which has incorporated therein a blooming system comprising:

a cationic quaternary ammonium surfactant;
an anionic carboxylated alcohol alkoxylate surfactant;
a surfactant compatibilizing agent; and,
water.

3. The composition according to claim 1 which comprises:

pine oil in an amount of from 0.01 - 3%wt., preferably 0.01 - 2.5% by weight, but most preferably 0.75-1.5%wt.l;

at least one pine oil solubilizing agent in an amount of to 15% and less by weight, preferably 0.01-10% by weight, and most preferably in an amount of 0.1-5% by weight and a blooming system which includes:

a cationic quaternary ammonium surfactant;
an anionic carboxylated alcohol alkoxylate surfactant;
a surfactant compatibilizing agent; and,
water.

4. The composition according to claim 1 which comprises:

pine oil, in amount of 0.1-5% by weight, preferably in amounts of 0.1 - 4% by weight, but most preferably in amount of between 2 - 4% by weight;

at least one pine oil solubilizing agent effective in enhancing the miscibility of the pine oil constituent in water which may be present in any effective amount found but desirably is present in amounts of up to about 15% by weight, preferably in amounts of 0.1 - 15% by weight, but most preferably from 5 - 15% by weight
5 a nonionic surfactant with a cloud point of 20°C or less;
and, water.

5. A germicidal composition according to claim 1.

10 6. An aqueous blooming type, hard surface cleaning composition concentrate substantially as described herein with reference to the Examples.

7. A cleaning composition which comprises the aqueous blooming type, hard surface cleaning composition concentrate according to any preceeding claim diluted in a larger volume of water.

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8. A process for process for treating a hard surface requiring cleaning which comprises the process step of:

contacting the hard surface with an aqueous blooming type, hard surface cleaning composition concentrate according to any preceeding claim an amount effective for providing
20 cleaning treatment.

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9. A process for process for treating a hard surface requiring cleaning which comprises the process step of:

forming an aqueous dilution of the composition according to claim 1 in a larger volume of water, and thereafter,

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applying the said aqueous dilution in an amount effective for providing cleaning treatment.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/12613

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D1/65 C11D3/48 C11D3/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 268 873 A (BENCKISER GMBH JOH A) 1 June 1988 see claim 1 ---	1,2,5,6
A	EP 0 651 048 A (EASTMAN KODAK CO) 3 May 1995 see claims ---	1,5,8
A	EP 0 288 689 A (AMERICAN CYANAMID CO) 2 November 1988 see claims 1-4 ---	1,3,5
A	DE 23 49 323 A (HENKEL & CIE GMBH) 10 April 1975 see page 8, line 11 - line 32; claims 1-6 -----	1,2,5

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

5 December 1996

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/LJ 96/12613

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EP-A-0288689	02-11-88	US-A- 4867898	19-09-89
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		ZA-A- 8802041	19-09-88
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